

# **Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration**

**LG501**

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## Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration

### **1.0 SCOPE AND APPLICATION**

- 1.1 This method is applicable to surface waters and other "clean" water.
- 1.2 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure, provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.
- 1.3 The sensitivity of the method is approximately 0.1 mg/L.

### **2.0 SUMMARY OF METHOD**

- 2.1 The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide,  $\text{Mn}(\text{OH})_2$  combines with the dissolved oxygen (D.O.) in the sample to form a brown precipitate, manganic hydroxide,  $\text{MnO}(\text{OH})_2$ . Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate.
- 2.2 The reagents are prepared prior to the cruise at the support laboratory.
- 2.3 During the first day of the cruise prior to sampling, the 0.0075 N thiosulfate is prepared and standardized according to Sections 6.7 and 6.12. Reagents #1 and #2 are checked according to Sections 6.2 and 6.3 to determine their background oxidation capability. If there is a color, titrate with the 0.0075 titrant until clear and record one half the volume as  $\text{MnSO}_4$  blank and/or alkaline iodide blank. To verify that the procedure is operational, a high control check or spike is run in duplicate. The results should agree within 0.2 mg/L and should agree with the calculated value within 0.5 mg/L.

### **3.0 SAMPLE HANDLING AND PRESERVATION**

- 3.1 Samples are collected and transferred to 60-mL glass BOD bottles. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen.
- 3.2 D.O. must be determined immediately at the collection site. There is no holding time.

### **4.0 INTERFERENCES**

- 4.1 There are numerous interferences to the dissolved oxygen test, including oxidizing and reducing agents. For clean samples, such as lake water, chemical interferences are minimal and ignored.

## **5.0 APPARATUS**

- 5.1 Incubation bottles, 60-mL, such as Wheaton Scientific #227494
- 5.2 Burets, 25-mL, accurate to 0.05 mL
- 5.3 Volumetric flask, 1-L
- 5.4 Graduated cylinders, 500-mL and 100-mL
- 5.5 Pipettors, 0.4-mL, such as Eppendorf
- 5.6 Propipetors with plastic parts for Reagents #1 and #2, 0.4-mL delivery volume

## **6.0 REAGENTS**

- 6.1 Reagent water: Throughout this SOP "water" is understood to mean reagent water, unless otherwise specified, and "dilute," used as a verb, means dilute with reagent water.
- 6.2 Manganese sulfate solution: Dissolve 120 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 100 g  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ , or 91 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in water and dilute to 250 mL in a graduated cylinder or bottle marked at 250 mL. Test this solution by adding 0.8 mL to a solution containing 100 mL of water, 10 mL 10% sulfuric acid, 10 mL 10% KI and starch indicator. There should be no color.
- 6.3 Alkaline azide reagent: Dissolve 125 g NaOH (or 175 g KOH) and 33.8 g NaI (or 37.5 g KI) in water and dilute to 250 mL in a graduated cylinder or bottle marked at 250 mL. To this solution add 2.5 g sodium azide,  $\text{NaN}_3$ , which has been dissolved in 10 mL of water. Test this solution by adding 0.8 mL to a solution containing 100 mL of water, 10 mL 10% sulfuric acid and starch indicator. There should be no color.
- 6.4 Sulfuric acid, concentrated.
- 6.5 Starch indicator solution: Dissolve 2 g laboratory grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 mL hot water.
- 6.6 Sodium thiosulfate stock solution, 0.0375 N: Dissolve 9.3075 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water and add 0.6 g NaOH or 15 mmol and dilute to one liter.
- 6.7 Sodium thiosulfate standard titrant, 0.0075 N: Dilute 200 mL (or an appropriate volume) of stock solution (6.6) to 1 liter. Standardize according to Section 6.12. Prepare weekly.
- 6.8 Potassium biiodate stock solution, 0.15 N: Dissolve 4.873 g of  $\text{KH}(\text{IO}_3)_2$  (previously dried at 103°C for two hours) in water and dilute to 1 liter.
- 6.9 Potassium biiodate working standard, 0.0375 N: Dilute 250 mL of stock solution (6.8) to 1 liter.
- 6.10 Potassium iodide solution, 10%: Dissolve 10 g of KI in water and dilute to 100 mL.
- 6.11 Sulfuric acid, 10%: Carefully add 50 mL of concentrated sulfuric acid to 460 mL of water.

- 6.12 Standardization of 0.0075 N sodium thiosulfate: Add 10 mL of 10% KI (6.10) and 10 mL of 10%  $\text{H}_2\text{SO}_4$  (6.11) to 100 mL of water, followed by 4 mL of potassium biiodate working standard (6.9). Place in the dark for 5 minutes and then titrate with sodium thiosulfate standard titrant (6.7) to a pale straw color. Add 1-2 mL of starch solution (6.5) and continue the titration dropwise until the blue color disappears. Run in duplicate. Titrant necessary should be 20 mL.
- 6.12.1 If the titrant (sodium thiosulfate) volume is greater than 20 mL, it is too weak. The following equation is used to calculate the volume of 0.0375 N sodium thiosulfate needed to adjust and increase the concentration of the titrant to 0.0075 N:  $(\text{titrant}-20) \times 200/20$ . The calculated value derived from this equation is the volume of stock sodium thiosulfate that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate).
- 6.12.2 If the titrant (sodium thiosulfate) volume is less than 20 mL, it is too strong. The following equation is used to calculate the volume of water needed to adjust and decrease the concentration of the titrant to 0.0072 N:  $(20-\text{titrant}) \times 1000/20$ . The calculated value derived from this equation is the volume of water that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate).
- 6.12.3 After adjusting the concentration of the titrant, standardize the solution again. Repeat procedures outlined in Section 6.12, if necessary.

## **7.0 PROCEDURE**

- 7.1 The sample is transferred from the Niskin bottle by inserting the Niskin drain tube to the bottom of a 60-mL BOD bottle and allowing the sample water to overflow long enough to displace at least three volumes (180 mL).
- 7.2 Within ten minutes, using the propipetors, add 0.4 mL of the manganous sulfate solution, followed by 0.4 mL of the alkaline iodide-azide solution (6.2) allowing the solutions to run down the neck of the bottle. Stopper the bottle, being careful to exclude any air bubbles, and mix well by repeated inversion of the bottle. When the precipitate settles to clear the upper 1/3 of the bottle, mix again by repeated inversion. After a second settling period produces an upper 1/3 of the bottle free of floc, remove the stopper and add 0.4 mL of concentrated sulfuric acid by allowing the acid to run down the neck of the bottle. Restopper, again being careful to exclude air bubbles, and mix by repeated inversion. Complete the analysis within 45 minutes of the acid addition.
- 7.3 Transfer the bottle contents to a 150- or 200-mL beaker and titrate with 0.0075 N thiosulfate solution (6.7) to a pale straw color. Add 1 to 2 mL of starch indicator and continue the titration to the first disappearance of the blue color. Record the mL of titrant and the volume of the BOD bottle.
- 7.4 Occasionally, a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of  $\text{H}_2\text{SO}_4$  will effect dissolution.

## **8.0 CALIBRATIONS**

- 8.1 Dissolved oxygen in mg/L is read directly from the buret if the BOD bottle is 60.8 mL, or else the value is the buret reading times 60.8 divided by the BOD bottle volume. Record the volume of titrant and the BOD bottle volume.
- 8.2 Calculation of DO from temperature and barometric pressure.

- 8.2.1 Prepare a saturated (with oxygen) water sample by vigorously shaking (10 - 15 times) a rigid plastic 960-mL bottle half full of reagent water or sample water. Obtain a barometer reading and measure the temperature of the saturated water. The following table can be used to obtain the mg/L DO at 760 mm Hg. Most barometers are corrected to sea level from their present elevation. This means that the true barometric pressure is equal to the barometric reading minus 18 mm (0.71 in) for Lakes Michigan, Erie, and Huron. The barometer reading in inches of mercury can be converted to millimeters by multiplying by 25.4, from millibars to millimeters of mercury, multiply by 0.75006.
- 8.2.2 Extrapolate DO solubility between whole temperature units for temperatures to 0.1°C. A table displaying extrapolated oxygen solubility in water to 0.1°C is located in **Attachment A** of this standard operating procedure.
- 8.2.3 Adjust the extrapolated DO solubility for barometric pressure by direct ratio, i.e.,

$$\frac{\text{Extrapolated solubility} \times (\text{corrected barometric pressure} - 18\text{mm})}{760 \text{ mm}}$$

- 8.2.4 The true or actual barometric pressure is reportedly available on the *R/V Lake Guardian* from the NEMA stream. The corrected to sea level values for Lake Michigan are also available from the barometer on the flying bridge. The current sea level pressure can also be obtained off the internet from the [www.nws.noaa.gov](http://www.nws.noaa.gov) current weather conditions aviation at the local airports.

**Oxygen Solubility**  
**Salinity less than 0.1 g/L, 760 mm Hg barometric pressure**

Temp	DO	Temp	DO	Temp	DO	Temp	DO	Temp	DO
0	14.62	6	12.45	12	10.78	18	9.47	24	8.42
1	14.22	7	12.14	13	10.54	19	9.28	25	8.26
2	13.83	8	11.84	14	10.31	20	9.09	26	8.11
3	13.46	9	11.56	15	10.08	21	8.91	27	7.97
4	13.11	10	11.29	16	9.87	22	8.74	28	7.83
5	12.77	11	11.03	17	9.66	23	8.58	29	7.69

## 9.0 QUALITY CONTROL

**Note:** In 2003, Winkler analyses are being performed by two similar procedures, the only difference being that with one procedure the DO reagent #2 contains azide and with the other procedure, reagent #2 does not contain azide. Each sample is analyzed using both procedures and in the following discussion, duplicate refers to the results from the two procedures, one duplicate from one procedure the other duplicate from the other procedure. The corrected titration values should agree within 0.2 mg/L. Duplicate azide and duplicate non-azide are to be performed on the following samples:

- 1) in the spring, all samples from the master stations;
- 2) the B-1 samples on each DO survey at Lake Erie Stations 73 and 78; and
- 3) all B-1 samples on the August DO central basin survey (see Appendix D) .

For tracking purposes, the "S"(RFS) and "C" (LDn) sample should refer to the samples with the azide. New IDs "E"(RFS)(ALT lab remark code) and "A"(LDn)(ALT lab remark code) will be used for the non-azide method.

- 9.1 The two aliquots for duplicate analysis are taken directly from the Niskin bottle. On regular surveys, duplicate analyses of a surface or B-10 are performed at each Master Station. On DO surveys, duplicate analyses are performed at the surface and at the B-1 depth at each Lake Erie Central Basin station.
- 9.2 At the beginning of each DO survey and daily thereafter, a saturated lake water sample is used to check for interferences or method error as described in Section 8.2. If the calculated value and the average determined value differ by more than 0.5 mg/L, the same test should be performed on reagent water. If a similar deviation is obtained on reagent water, then it can be assumed that method error is the problem, and corrective action should be initiated such as; re-standardize the titrant, check that the procedure is being performed correctly, etc.
- 9.3 The following QC samples must be prepared and analyzed at the minimum frequency indicated.

QC Type	Frequency	Acceptance Criteria
Lab Duplicate (LD1)	Each Master Station	Absolute Difference < 0.2 mg/L
	DO Surveys: All SRF and B-1 samples	
Lab Accuracy Check, Saturated Sample (Sections 9.2 and 10.2)	At the beginning of each lake of a regular survey	± 0.5 mg/L, compared to theoretical
	DO Surveys: At the beginning and once per shift	

### 9.4 Assessment

- 9.4.1 The analyst must compare analytical results to the acceptance criteria listed in Section 9.3 to identify QC failures. If the results are outside the acceptance criteria, the analyst

should first review their calculations for errors and if none are identified, they must follow the corrective action procedures listed in Section 9.5.

## 9.5 Corrective Actions

9.5.1 Corrective action procedures will often be handled at the bench level by the analyst, who reviews the procedure for possible errors, checks calculations and any other potential sources of error. If the problem persists or cannot be identified, the matter must be referred to the Chief Scientist for further investigation. Depending upon the Chief Scientist's evaluation, the analyst may or may not be required to prepare and re-run the samples again. Once a decision is made, full documentation of the corrective action procedures and assessment of the final result must be filed with the WQS QM Technical Lead (Marvin Palmer) or the GLNPO QM.

## 9.6 Data Reporting/Recording

9.6.1 The analyst is responsible for identifying all failed QC samples in the remarks column of the Laboratory reporting forms. If analyses are being conducted onboard, the analyst should document the QC information on the hard-copy Field Information Recording Forms (Appendix H).

## 10.0 SUMMARY

- 10.1 Thiosulfate standardization - at the beginning of a Multi-Lake Survey or a DO Survey.
- 10.2 Saturated water sample is analyzed in duplicate and compared with the theoretical value (9.2 and 7) - at the beginning of a multi-lake survey and once per shift on DO surveys.
- 10.3 Laboratory duplicate samples are analyzed - at least one depth at each Master Station, Surface and B-1 at each station on DO surveys.
- 10.4 Comparison of SB 911 and SB 25 - at least one station per survey on which both are available. Document the results of the DO reading comparison at the 5 m depth on the CS check sheet (Appendix L).

## 11.0 SAFETY AND WASTE HANDLING

- 11.1 Refer to GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) and individual instrument procedural operations manuals for specific details on applicable 1) personal health and safety issues; 2) instrumental, chemical, and waste handling procedures; and 3) accident prevention. This applies to all EPA personnel, EPA contractors or federal, state, or local government agencies, and persons who operate or are passengers onboard US EPA GLNPO vessels during all activities and surveys.
- 11.2 All containers storing reagents, standards, controls, blanks, and wastes used in the laboratory must be properly identified through appropriate labeling and hazard definition.
- 11.3 Every chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Please refer to Appendix L in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) for more detailed



descriptions of the potential risks associated with any chemicals used in this method. It is good laboratory practice to wear a lab coat, safety goggles and gloves at all times.

- 11.4 It is the responsibility of the user of this method to comply with relevant chemical disposal and waste regulations as cited in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended). All applicable safety and waste handling rules are to be followed. Good technique includes minimizing contaminated waste.
- 11.5 Over-board discharges of chemical wastes are forbidden.

## **12.0 REFERENCES**

- 12.1 "Methods for Chemical Analysis of Water and Wastes," USEPA Publication #600/4-79-020, March, 1979.
- 12.2 "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 18<sup>th</sup> Edition, 1992.

## ATTACHMENT A

Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius																			
0 to 10 °C, by 1 °C Increments																			
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
0	14.62	1	14.22	2	13.83	3	13.46	4	13.11	5	12.77	6	12.45	7	12.14	8	11.84	9	11.56
1	14.22	2	13.83	3	13.46	4	13.11	5	12.77	6	12.45	7	12.14	8	11.84	9	11.56	10	11.29
0 to 10 °C, by 0.1 °C Increments																			
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
0.0	14.62	1.0	14.22	2.0	13.83	3.0	13.46	4.0	13.11	5.0	12.77	6.0	12.45	7.0	12.14	8.0	11.84	9.0	11.56
0.1	14.58	1.1	14.18	2.1	13.79	3.1	13.43	4.1	13.08	5.1	12.74	6.1	12.42	7.1	12.11	8.1	11.81	9.1	11.53
0.2	14.54	1.2	14.14	2.2	13.76	3.2	13.39	4.2	13.04	5.2	12.71	6.2	12.39	7.2	12.08	8.2	11.78	9.2	11.51
0.3	14.50	1.3	14.10	2.3	13.72	3.3	13.36	4.3	13.01	5.3	12.67	6.3	12.36	7.3	12.05	8.3	11.76	9.3	11.48
0.4	14.46	1.4	14.06	2.4	13.68	3.4	13.32	4.4	12.97	5.4	12.64	6.4	12.33	7.4	12.02	8.4	11.73	9.4	11.45
0.5	14.42	1.5	14.03	2.5	13.65	3.5	13.29	4.5	12.94	5.5	12.61	6.5	12.30	7.5	11.99	8.5	11.70	9.5	11.43
0.6	14.38	1.6	13.99	2.6	13.61	3.6	13.25	4.6	12.91	5.6	12.58	6.6	12.26	7.6	11.96	8.6	11.67	9.6	11.40
0.7	14.34	1.7	13.95	2.7	13.57	3.7	13.22	4.7	12.87	5.7	12.55	6.7	12.23	7.7	11.93	8.7	11.64	9.7	11.37
0.8	14.30	1.8	13.91	2.8	13.53	3.8	13.18	4.8	12.84	5.8	12.51	6.8	12.20	7.8	11.90	8.8	11.62	9.8	11.34
0.9	14.26	1.9	13.87	2.9	13.50	3.9	13.15	4.9	12.80	5.9	12.48	6.9	12.17	7.9	11.87	8.9	11.59	9.9	11.32
1.0	14.22	2.0	13.83	3.0	13.46	4.0	13.11	5.0	12.77	6.0	12.45	7.0	12.14	8.0	11.84	9.0	11.56	10.0	11.29
10 to 20 °C, by 1 °C Increments																			
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
10	11.29	11	11.03	12	10.78	13	10.54	14	10.31	15	10.08	16	9.87	17	9.66	18	9.47	19	9.28
11	11.03	12	10.78	13	10.54	14	10.31	15	10.08	16	9.87	17	9.66	18	9.47	19	9.28	20	9.09
10 to 20 °C, by 0.1 °C Increments																			
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
10.0	11.29	11.0	11.03	12.0	10.78	13.0	10.54	14.0	10.31	15.0	10.08	16.0	9.87	17.0	9.66	18.0	9.47	19.0	9.28
10.1	11.26	11.1	11.01	12.1	10.76	13.1	10.52	14.1	10.29	15.1	10.06	16.1	9.85	17.1	9.64	18.1	9.45	19.1	9.26
10.2	11.24	11.2	10.98	12.2	10.73	13.2	10.49	14.2	10.26	15.2	10.04	16.2	9.83	17.2	9.62	18.2	9.43	19.2	9.24
10.3	11.21	11.3	10.96	12.3	10.71	13.3	10.47	14.3	10.24	15.3	10.02	16.3	9.81	17.3	9.60	18.3	9.41	19.3	9.22
10.4	11.19	11.4	10.93	12.4	10.68	13.4	10.45	14.4	10.22	15.4	10.00	16.4	9.79	17.4	9.58	18.4	9.39	19.4	9.20
10.5	11.16	11.5	10.91	12.5	10.66	13.5	10.43	14.5	10.20	15.5	9.98	16.5	9.77	17.5	9.57	18.5	9.38	19.5	9.19
10.6	11.13	11.6	10.88	12.6	10.64	13.6	10.40	14.6	10.17	15.6	9.95	16.6	9.74	17.6	9.55	18.6	9.36	19.6	9.17
10.7	11.11	11.7	10.86	12.7	10.61	13.7	10.38	14.7	10.15	15.7	9.93	16.7	9.72	17.7	9.53	18.7	9.34	19.7	9.15
10.8	11.08	11.8	10.83	12.8	10.59	13.8	10.36	14.8	10.13	15.8	9.91	16.8	9.70	17.8	9.51	18.8	9.32	19.8	9.13
10.9	11.06	11.9	10.81	12.9	10.56	13.9	10.33	14.9	10.10	15.9	9.89	16.9	9.68	17.9	9.49	18.9	9.30	19.9	9.11
11.0	11.03	12.0	10.78	13.0	10.54	14.0	10.31	15.0	10.08	16.0	9.87	17.0	9.66	18.0	9.47	19.0	9.28	20.0	9.09

<b>Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius</b>																	
<b>20 to 29 °C, by 1 °C Increments</b>																	
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
20	9.09	21	8.91	22	8.74	23	8.58	24	8.42	25	8.26	26	8.11	27	7.97	28	7.83
21	8.91	22	8.74	23	8.58	24	8.42	25	8.26	26	8.11	27	7.97	28	7.83	29	7.69
<b>20 to 29 °C, by 0.1 °C Increments</b>																	
T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
20.0	9.09	21.0	8.91	22.0	8.74	23.0	8.58	24.0	8.42	25.0	8.26	26.0	8.11	27.0	7.97	28.0	7.83
20.1	9.07	21.1	8.89	22.1	8.72	23.1	8.56	24.1	8.40	25.1	8.24	26.1	8.10	27.1	7.96	28.1	7.82
20.2	9.05	21.2	8.88	22.2	8.71	23.2	8.55	24.2	8.39	25.2	8.23	26.2	8.08	27.2	7.94	28.2	7.80
20.3	9.04	21.3	8.86	22.3	8.69	23.3	8.53	24.3	8.37	25.3	8.21	26.3	8.07	27.3	7.93	28.3	7.79
20.4	9.02	21.4	8.84	22.4	8.68	23.4	8.52	24.4	8.36	25.4	8.20	26.4	8.05	27.4	7.91	28.4	7.77
20.5	9.00	21.5	8.83	22.5	8.66	23.5	8.50	24.5	8.34	25.5	8.19	26.5	8.04	27.5	7.90	28.5	7.76
20.6	8.98	21.6	8.81	22.6	8.64	23.6	8.48	24.6	8.32	25.6	8.17	26.6	8.03	27.6	7.89	28.6	7.75
20.7	8.96	21.7	8.79	22.7	8.63	23.7	8.47	24.7	8.31	25.7	8.16	26.7	8.01	27.7	7.87	28.7	7.73
20.8	8.95	21.8	8.77	22.8	8.61	23.8	8.45	24.8	8.29	25.8	8.14	26.8	8.00	27.8	7.86	28.8	7.72
20.9	8.93	21.9	8.76	22.9	8.60	23.9	8.44	24.9	8.28	25.9	8.13	26.9	7.98	27.9	7.84	28.9	7.70
21.0	8.91	22.0	8.74	23.0	8.58	24.0	8.42	25.0	8.26	26.0	8.11	27.0	7.97	28.0	7.83	29.0	7.69